Diffusion in Linear Porous Media With Periodic Entropy Barriers: A Tube Formed by Contacting Spheres

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The problem of transport in quasi-one dimensional periodic structures has been studied recently by several groups [1-4]. Using the concept of "entropy barrier" [5] one can classify such structures based on the height of the entropy barrier. Structures with high barriers are formed by chambers, which are weakly connected with each other because they are connected by small apertures. To escape from such a chamber a diffusing particle has to climb a high entropy barrier to find an exit that takes a lot of time [6]. As a consequence, the particle intra-chamber lifetime, τ_{esc}, is much larger than its intra-chamber equilibration time, τ_{rel}, $\tau_{esc} >> \tau_{rel}$. When the aperture is not small enough, the intra-chamber escape and relaxation times are of the same order and the hierarchy fails. This is the case of low entropy barriers. Transport in this case is analyzed in Refs. [1-3], while Ref. [4] is devoted to diffusion in the case of high entropy barriers.

In this paper we study diffusion in a tube formed by periodic contacting spherical cavities of radius, R, (Fig. 1) over the entire range of the entropy barrier height. On times when the mean squared displacement of a diffusing particle is much greater than the tube period, l, the particle motion can be characterized by an effective diffusion constant, D_{eff}, which is smaller than the particle diffusion constant, D, in space with no constrains. When the tube period increases, the radius a of the circular aperture connecting neighboring cavities decreases, $a = \sqrt{R^2 - (l^2/4)}$, $0 < l < 2R$. As a result, the entropy barrier increases, and the ratio D_{eff}/D gets smaller. One can find D_{eff} analytically for high and low entropy barriers. For high entropy barriers D_{eff} has been derived in Ref. [4]. Here we derive D_{eff} for low entropy barriers. We also run Brownian dynamics simulations to find D_{eff} as a function of the ratio a/R and to compare the numerical results with those predicted by different analytical expressions. The major goal of our analysis is to establish the range of applicability of different approximate expression for D_{eff}.

For high entropy barriers (small apertures, $a << R$) Berezhkovskii, Zitserman, and Shvartsman (BZS) derived the following expression for the effective diffusion constant,

$$D_{eff}^{BZS} = \frac{6Da}{\pi R} \tag{1}$$

In the opposite limiting case of low entropy barrier, i.e., when $(R-a) << R$, one can find D_{eff} by approximately reducing the three-dimensional problem of diffusion in the tube of varying cross section to an effective one-dimensional problem of diffusion along the tube axis. Significant progress in understanding the reduction has been made in recent years [5, 7-9]. Directing the x-axis along the center line of the tube one can write an approximate one-dimensional effective diffusion equation as

$$\frac{\partial c(x,t)}{\partial t} = \frac{\partial}{\partial x}\left\{D(x)A(x)\frac{\partial}{\partial x}\left[\frac{c(x,t)}{A(x)}\right]\right\}, \quad (2)$$

where D(x) is a position-dependent diffusion coefficient, $A(x) = \pi[r(x)]^2$ is the cross-section area of the tube of radius $r(x)$, and $c(x,t)$ is the effective one-dimensional concentration of the diffusing particles at given x, which is related to the three-dimensional concentration $C(x,y,z,t)$ by

$$c(x,t) = \int_{A(x)} C(x,y,z,t)dydz. \quad (3)$$

Equation (2) with position-independent diffusion coefficient, $D(x) = D$, is known as the Fick-Jacobs equation [10]. Zwanzig (Zw) derived an expression for $D(x)$ assuming that the tube radius, $r(x)$, is a slowly varying function, $|r'(x)| << 1$, [5],

$$D_{Zw}(x) = \frac{D}{1 + r'(x)^2/2}. \quad (4)$$

Reguera and Rubí (RR) generalized this result [7]. Based on heuristic arguments they suggested

$$D_{RR}(x) = \frac{D}{\sqrt{1 + r'(x)^2}} \quad (5)$$

Equation (2) can be considered as the Smoluchowski equation for diffusion in the entropy potential $U(x)$ defined as

$$U(x) = -k_B T \ln \frac{A(x)}{A(x_0)}, \qquad (6)$$

where k_B and T are the Boltzmann constant and the absolute temperature, and $U(x)$ at $x = x_0$ is taken to be zero, $U(x_0) = 0$. Potentials $U(x)$ with high and low entropy barriers are shown in Fig. 1. Since our system is periodic, it follows from Eqs. (4)-(6) that both $U(x)$ and $D(x)$ are periodic functions of x, $U(x+l) = U(x)$ and $D(x+l) = D(x)$. Therefore, we can find D_{eff} using the Lifson-Jackson formula [11], which is an exact result for the one-dimensional Smoluchowski equation with periodic $U(x)$ and $D(x)$. According to this formula D_{eff} is given by

$$D_{eff}^{-1} = \left\langle \left[D(x) A(x) \right]^{-1} \right\rangle \left\langle A(x) \right\rangle, \qquad (7)$$

where $\langle f(x) \rangle = \frac{1}{l} \int_0^l f(x) dx$. We use Eq. (7) to obtain three different expressions for D_{eff}.

Assuming that $D(x) = D$ we find D_{eff}^{FJ}, which corresponds to the Fick-Jacobs (FJ) equation,

$$\frac{D}{D_{eff}^{FJ}} = \left\langle \frac{1}{A(x)} \right\rangle \left\langle A(x) \right\rangle = \frac{2 + (a/R)^2}{6\sqrt{1-(a/R)^2}} \ln \frac{1+\sqrt{1-(a/R)^2}}{1-\sqrt{1-(a/R)^2}}. \qquad (8)$$

Using $D_{Zw}(x)$, Eq. (4), we obtain D_{eff}^{Zw} given by

$$\frac{D}{D_{eff}^{ZW}} = \frac{D}{D_{eff}^{FJ}} + \frac{1}{2} \left\langle \frac{r'(x)^2}{A(x)} \right\rangle \left\langle A(x) \right\rangle = \frac{2 + (a/R)^2}{12} \left[\frac{1}{(a/R)^2} + \frac{3}{2\sqrt{1-(a/R)^2}} \ln \frac{1+\sqrt{1-(a/R)^2}}{1-\sqrt{1-(a/R)^2}} \right]. \qquad (9)$$

Respectively, $D_{RR}(x)$ in Eq. (5) leads to D_{eff}^{RR} given by

$$\frac{D}{D_{eff}^{RR}} = \left\langle \frac{\sqrt{1-r'(x)^2}}{A(x)} \right\rangle \langle A(x) \rangle = \frac{2}{3(a/R)}. \tag{10}$$

The results in Eqs. (8)-(10) were obtained assuming that the entropy barrier is low and the difference $R-a$ is small compared to R. It is interesting to compare the behavior predicted by these equations in the opposite limit when $a \to 0$ and the entropy barrier is high, with D_{eff}^{BZS} in Eq. (1), which is asymptotically exact in this limit. Comparison shows that $D_{eff}^{FJ}/D_{eff}^{BZS} \to \infty$, $D_{eff}^{Zw}/D_{eff}^{BZS} \to 0$, $D_{eff}^{RR}/D_{eff}^{BZS} \to \pi/4$. Thus, D_{eff}^{RR} in Eq. (10) is a good candidate for a unique formula that covers the entire range of a/R, $0 < a/R < 1$, while both, D_{eff}^{FJ} and D_{eff}^{Zw} fail as $a/R \to 0$.

We compare different expressions for D_{eff}, Eqs. (1), (8)-(10), with D_{eff}^{sim} found in Brownian dynamics simulations. Numerically we compute the mean squared displacement along the channel axis of 2.5×10^4 particles as a function of time, $\langle \Delta x^2(t) \rangle = \langle [x(t)-x(0)]^2 \rangle$, assuming that the particle starting points are uniformly distributed over the cavity. We determine D_{eff}^{sim} from the long-time behavior of $\langle \Delta x^2(t) \rangle$. The results presented in Fig. 2 show that D_{eff}^{sim} is in excellent agreement with D_{eff}^{BZS} for $a/R < 0.1$, reasonably well described by both D_{eff}^{BZS} and D_{eff}^{RR} for $a/R = 0.2$; and close to D_{eff}^{RR} for $a/R \geq 0.3$.

To summarize, D_{eff}^{RR} in Eq. (10) found on the basis of the generalized Fick-Jacobs equation, Eq. (2), with $D(x)$ given by the Reguera-Rubí formula, Eq. (5), provides a reasonably good approximation for D_{eff} over the entire range of the size of the aperture. For small windows (high entropy barriers) D_{eff}^{sim} found numerically is in excellent agreement with D_{eff}^{BZS} in Eq. (1). We hope that the results of our analysis will be of use when interpreting experiments on controlled drug release and migration in porous media.

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References

[1] D. Reguera, G. Schmid, P. S. Burada, J. M. Rubí, P. Reimann, and P. Hänggi, *Phys. Rev. Lett.* **96**, 130603 (2006); P. S. Burada, G. Schmid, D. Reguera, J. M. Rubí, and P. Hänggi, *Phys. Rev. E.* **75**, 051111 (2007).

[2] B. Q. Ai and L. G. Liu, , *Phys. Rev. E.* **74**, 051114 (2006); B. Q. Ai, H. Z. Xie, and L. G. Liu, , *ibid* **75**, 061126 (2007); B. Q. Ai and L. G. Liu, *J. Chem. Phys.* **126**, 204706 (2007); **128**, 024706 (2008).

[3] E. Yariv and K. D. Dorfman, *Phys. Fluids* **19**, 037101 (2007); N. Laachi, M. Kenward, E. Yariv, and K. D. Dorfman, *Europhys. Lett*. **80**, 50009 (2007).

[4] A. M. Berezhkovskii, V. Yu. Zitserman, and S. Y. Shvartsman, *J. Chem. Phys.* **118**, 7146 (2003); **119**, 6991 (2003).

[5] R. Zwanzig, *J. Phys.Chem.* **96**, 3926 (1992).

[6] I. V. Grigoriev, Yu. A. Makhnovskii, A. M. Berezhkovskii, and V. Yu. Zitserman, *J. Chem. Phys.*. **116**, 9574 (2002).

[7] D. Reguera and J. M. Rubí, *Phys. Rev. E.* **64**, 061106 (2001).

[8] P. Kalinay and J. K. Percus, *J. Chem. Phys.* **122**, 204701 (2005); *Phys. Rev. E* **72**, 061203 (2005); *ibid.* **74**, 041203 (2006); *J. Stat. Phys.* **123**, 1059 (2006).

[9] A. M. Berezhkovskii, M. A. Pustovoit, and S. M. Bezrukov, *J. Chem. Phys.* **126**, 134706 (2007).

[10] M. H. Jacobs, "Diffusion Processes" (Springer, New York, 1967).

[11] S. Lifson and J. L. Jackson, *J. Chem. Phys.* **36**, 2410 (1962).

Figure Captions

Figure 1. Entropy potential for tubes with $(a/R)=0.1$ (panel(a)) and $(a/R)=0.5$ (panel(b)). The dimensionless heights of the entropy barriers, respectively, are $\Delta U/(k_B T)=2\ln 10\cong 4.6$ (panel(a)) and $\Delta U/(k_B T)=2\ln 2\cong 1.4$ (panel(b)).

Figure 2. Effective diffusion constants found numerically (circles) and predicted by Eqs. (1), (8)-(10) (solid curves). The insert shows the ratio of D_{eff}^{BZS} and D_{eff}^{RR} predicted by Eqs. (1) and (10), respectively, to D_{eff}^{sim}, from $(a/R)=0.025$ to $(a/R)=0.3$.

Figures

Figure 1a JCP

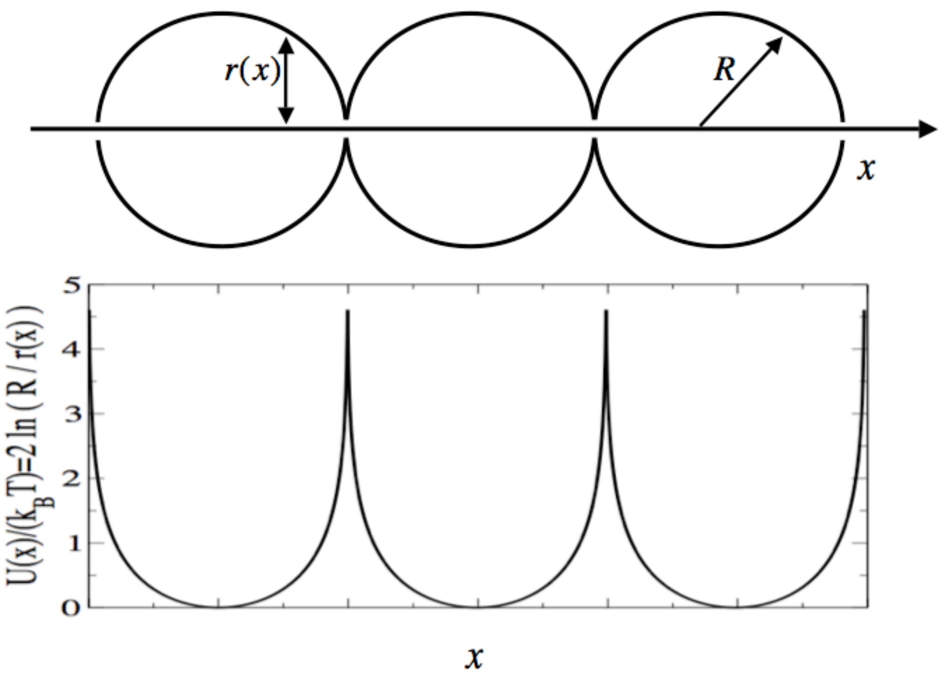


Figure 1b JCP

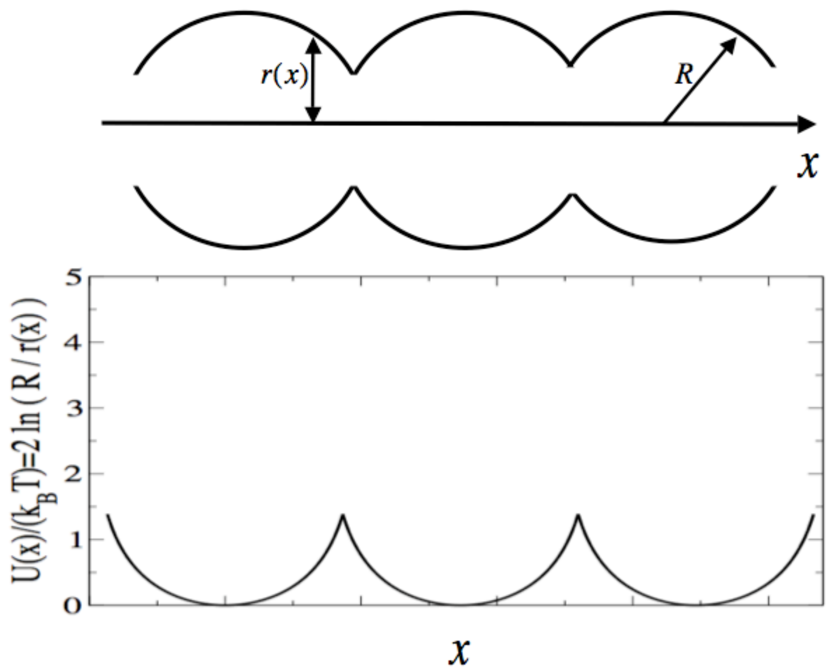
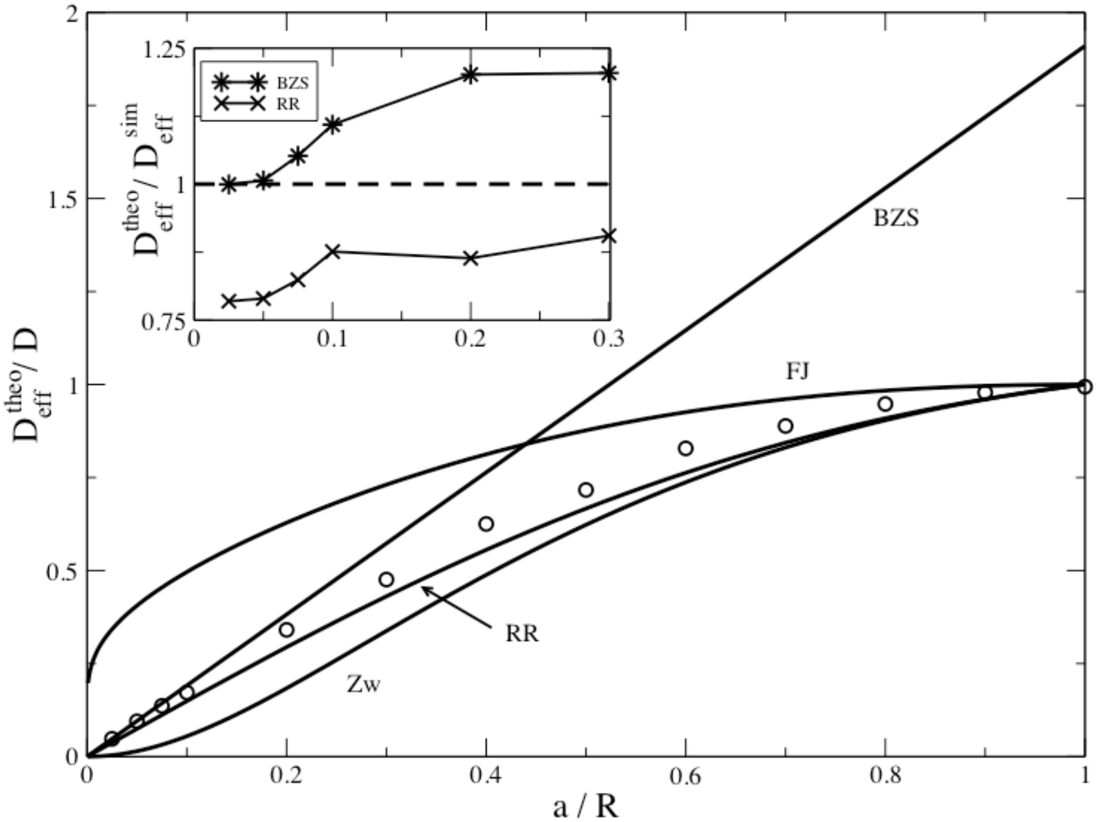


Figure 2 JCP



BZS
RR
1.25
1
0.75
0
0.1
0.2
0.3
$D_{eff}^{theo} / D_{eff}^{sim}$
BZS
FJ
RR
Zw
D_{eff}^{theo} / D
a / R
0
0.2
0.4
0.6
0.8
1
0.5
1.5
2